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FRAUNHOFER LINE-DEPTH SENSING APPLIED TO WATER*

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ABSTRACT

An experimental Fraunhofer Line Discriminator (FLD) is basically an airborne fluorometer, capable of quantitatively measuring the concentration of fluorescent substances dissolved in water. It must be calibrated against standards and supplemented by ground-truth data on turbidity and on approximate vertical distribution of the fluorescent substance. Quantitative use requires that it be known in advance what substance is the source of the luminescence emission. Qualitative sensing, or detection of luminescence is also possible, and does not have that limitation. The two approaches are fundamentally different, having different purposes, different applications, and different instruments. When used for sensing of Rhodamine WT dye in coastal waters and estuaries, the FLD is sensing in the spectral region permitting nearly maximum depth of light penetration. It should be nearly optimum for sensing in turbid estuaries such as Chesapeake Bay or San Francisco Bay.

THEORY OF THE FRAUNHOFER LINE-DEPTH METHOD AS APPLIED TO WATER

INTRODUCTION

An equation for luminescence coefficient (rho) (Stoertz, 1969) makes it appear independent of environmental factors such as sun angle. However testing of the FLD over a tank of fluorescent Rhodamine WT dye showed marked discrepancies in rho values, particularly during the late afternoon as the sun sank toward the horizon. Initial corrections for sun angle showed improvement in the records but large discrepancies remained. It became evident that the records from the instrument could not be interpreted in terms of luminescence intensities, or dye concentration, without first deriving a theoretical formula for function of the FLD as applied to water targets. A primary object of the first phase of the work was to test the performance of the instrument and determine whether it was malfunctioning, as a guide to design of an improved instrument. However since the instrument is specifically designed for use and testing over solutions of fluorescent rhodamine dye, a theoretical analysis of this was required initially. This is a unique application, consequently the formulation is largely theoretical, and will be refined or corrected in future operational tests. The formula, as first derived, contains three coefficients that are a function of dye concentration. These are a coefficient of sensitivity of the FLD to increments of dye, an attenuation coefficient for blue-green light by increments of dye, and a similar coefficient for attenuation of yellow luminescence emission by increments of dye. These are the critical coefficients that must be determined experimentally in order to

permit quantitative measurement of dye concentration by the FLD. The values of all coefficients used in the formulas have been estimated, but this is included in the second section of the report, the present section being purely theoretical.

Meaning of luminescence coefficient in relation to FLD

Rho, as measured by the FLD, was intended to represent the intrinsic luminosity of the target, independent of variations in the intensity of radiation stimulating the luminescence. Therefore it was intended to be a property of the target material, reproducible by measurements at different times and under different conditions. However, the value of rho, as measured by the FLD, has already been shown to be dependent on instrumental factors, so that it cannot strictly be said that rho is even directly proportional to intrinsic luminosity. In the following pages it is shown that rho measured over water targets is also dependent on a number of environmental factors unrelated to intrinsic luminosity of the fluorescent dye or other target material. Since the same problem will probably be encountered over land targets, though possibly to a lesser extent, and since there are unlikely to be more than a few FLD instruments in the near future, it will be convenient to think of rho as equivalent to FLD reading. It therefore has the same meaning as dial reading as used on a fluorometer and the term is so used throughout the remainder of this report. Consequently it has a numerical value equal to the reading on the recorder chart, and needs no units (i.e., is a ratio). This is consistent with the concept of the FLD as an airborne fluorometer.

Approximate meaning of rho as applied to a water target

The luminescence coefficient measured by the FLD over a water target represents the relative intensity of luminescence emission received through the lower portal from the direction of the target, expressed in relation to (i.e., divided by) the total intensity of incident sunlight and skylight received through the upper portal, with the added qualification:- as modified by temporal instrumental function and sensitivity to produce the final reading on the recorder chart.

To give this reading meaning in relation to the water surface it is necessary to assume two things: 1) that the sunlight and skylight received at the upper portal of the FLD is equal in intensity to the sunlight and skylight incident on the water surface; and 2) that the upward luminescence emission at the water surface is equal in intensity to that received at the lower portal of the FLD. For these assumptions to be approximately true requires that neither the instrument nor the water be partially or wholly in shadow, that the FLD be at a low altitude, and that the intervening atmosphere be reasonably free of absorptive or luminescent substances such as haze, fog, aerosols, or dust. These conditions should be fulfilled on a normal clear sunny day with the FLD mounted in a helicopter, but the altitude limit remains to be determined.

It should be emphasized that the preceeding paragraph applies to the water surface only, and the term water target was intentionally omitted. The water target must be considered to be the entire column of liquid sensed by the FLD, equivalent to the entire column from which detectable luminescence emanates. To give the reading of rho meaning with respect to the water target requires a restatement of the first paragraph. It will be presumed that the two assumptions listed above are valid.

Then the luminescence coefficient measured by the FLD over a water target represents the relative intensity of upward-trending luminescence emission reaching the water surface from the column sensed by the FLD, after being attenuated by absorption and scattering by all constituents of the column (suspended sediment, the water itself, the dye itself, and other coloring matter), and after being depleted by downward reflection from the water surface and by refraction due to surface roughness; the last two factors are neglected in subsequent derivation of a formula. This luminescence intensity is expressed in relation to the total intensity of sunlight and skylight incident on the water surface, in accord with the first paragraph. It is emphasized that this is not the intensity of light stimulating the luminescence of the column of liquid sensed by the FLD. Instead, the intensity used in computation of rho, and assumed equivalent to that at the water surface, is first depleted by refraction and reflection at the water surface and is then attenuated by absorption and scattering as described above, finally reaching the column sensed by the FLD.

The sensing of relative luminescence or concentration by the FLD

The rho value exactly as recorded by the FLD could be used as an indicator of luminescence, since any recorded value would be interpreted as indicative of luminescence. It could not, however, be used to interpret relative levels of luminescence reaching the water surface because the sunlight intensity measured by the FLD is not the same intensity that stimulated the luminescence. It would be erroneous to use the recorded rho values as a measure of relative levels of luminescence actually emitted by the dye, because this would introduce the additional errors of attenuation beneath the water surface, as explained above. The

error would be still greater if uncorrected rho values were used as a measure of relative levels of fluorescent dye concentration, because in this case the same rho value might be recorded for 1 foot of dye solution averaging 10 parts per billion as for 10 feet of solution averaging 1 part per billion. If the rho values were equated to relative amounts of fluorescent dye, without regard to concentration, the errors would be similar to those involved in equating them to relative levels of luminescence.

Therefore it is essential to use the instrument as a quantitative sensor whenever possible. Errors will be inevitable due to the host of variables, and the resulting dye concentrations might be thought of as relative values in this sense. Basically there are two types of sensing for which the Fraunhofer line-depth method is applicable - qualitative and quantitative. These two approaches are potentially of nearly equal value, just as the corresponding approaches to other fields of research. However they are fundamentally different, having different purposes, different (continued on page 6)

applications, and different instruments. If the present FLD were to be used for qualitative sensing of luminescence it might dispense with the upper portal and telescope, the light collector, one photo-multiplier, and might utilize a much simplified computer. However, these conclusions remain to be proven.

If it were desired to use the present FLD for high-altitude detection of luminescence, the following temporary modifications might be considered to accomplish this with maximum efficiency:

1) One of the following, whichever was simplest to accomplish:

a) Alteration of the beam-splitting ratio from 4:1 in favor of the lower portal to the reverse, but this modification is not likely to be feasible without considerable expense.

b) Rewiring of computer to calculate C/D ratio in place of B/A.

2) If a) was feasible, the instrument could be used in the reverse orientation, permitting the upper portal to view the ground and utilizing the present B/A ratio (to be termed C/D) as a measure of luminescence, when numerous targets were viewed in succession along a flight path. If b) was done the instrument would be used in the same way in the present orientation.

3) In either case, the alternate portal would be unneeded for light collection, hence it could serve as a convenient means for automatically monitoring a standard target to serve as a calibration of the sensitivity and adjustment of the instrument. This target would be used while monitoring either C or D if 1a) was done, alternatively A or B if 1b) was done.

Rationale used in deriving a formula for rho

It was concluded previously that the recorded value of rho is approximately equivalent to the intensity of the luminescence emission reaching the water surface, expressed in relation to the intensity of sunlight incident on the water surface. Presuming that the stated assumptions are true, the equivalents of these two light intensities are adequately measured by the FLD and therefore these actual intensities need not be considered in the formula. In order to relate rho to dye concentration or to the concentration of any other fluorescent substance in the water, however, it is necessary to account for all factors that cause a change in intensity of either the incident or the emitted light in their path from the water surface back to the water surface again.

Two alternative approaches are possible. In either one, rho must by definition be equated to intensity of luminescence emission reaching the water surface, expressed in relation to intensity of sunlight incident on the water surface. Since the ratio will be known, either parameter can arbitrarily be assigned a value of unity, and the equation written in terms of what changes in the other parameters are needed to produce the measured ratio. The major unknown in the problem is the subatomic process by which the incident light is absorbed by the fluorescent substance and then re-emitted in the form of luminescence. This will involve the luminescence efficiency of the substance, but also a number of other factors which cannot be readily quantified. Consequently the alternatives are to approach the major unknown from different directions and to account for the conversion of incident light into luminescence by a coefficient that will also embody all of the other

indeterminates and be solved periodically by means of a standard to relate instrumental sensitivity to increments of the fluorescent substance. Therefore the basic assumption must be that it will be known in advance what substance is the source of the luminescence emission, an assumption necessary in the quantitative use of any fluorometer.

In the first alternative the intensity of incident light at the water surface will be assumed to be unity. Percentage changes in the intensity of the incident light on its course through the water can be viewed as percentage changes in the potential luminescence emission from the surface, thus the intensity of neither the incident light nor the luminescence emission need be considered. A 5 percent loss of luminescence per meter will therefore have the same net effect as a 5 percent loss of incident light per meter, even though the latter is 100 times more intense, provided the rate of loss is operative over an equal distance. In this approach the problem of conversion into luminescence requires a coefficient equal to the intrinsic luminosity of an infinitely thin layer of a concentration increment of the luminescent liquid, divided by the thickness of such a layer and multiplied by the number of such concentration increments present in the solution.

The alternative approach would be to assume that the intensity of emitted light at the surface is unity. Then the equation would express the increases in light levels, traced backward through the water, to arrive at the required intensity of incident light needed to balance the equation. This approach would utilize growth rates instead of attenuation rates. Although fairly obvious, the alternative is mentioned to illustrate that the actual light intensities are immaterial at every stage,

and to emphasize the rationale used in omitting all symbols for light intensity throughout the report. The first approach is used in following derivations, for convenience, since the denominator will be unity.

Treatment of incident light at and above the air-water interface

The applicable geometry is shown on Figure 2. The only practicable approach has been to treat the incident light as parallel rays from the sun, since the FLD will be operable mainly in bright sunlight for quantitative sensing. Light reflected from clouds and sky has been ignored, although a certain amount will be collected at the light collector, introducing a small discrepancy. Another discrepancy is the fact that the light intensity measured by the FLD is that of yellow light at 5892Å, while the light stimulating the luminescence of rhodamine dye is blue-green light centering near 5540Å. The magnitude of this discrepancy will vary with time of day, angle of sunlight, and amount of light reflected from sky and clouds, so there seems to be no practical way to compensate for it. However this error seems to have been overlooked in the literature on the FLD.

Refraction at the water surface, in accord with Snell's Law is:

$$n = \frac{\sin i}{\sin j} = \frac{V_a}{V_w} = \frac{\sin(90° - \phi)}{\sin(90° - \theta)} = \frac{\cos\phi}{\cos\theta} \qquad (1)$$

in which: n = index of refraction of light in air with respect to water

i = angle of incidence from the normal

j = angle of transmission from the normal

V_a = velocity of light in air

V_w = velocity of light in water

ϕ = angle of sun above horizon

θ = refracted angle of sun's rays, measured downward from water surface

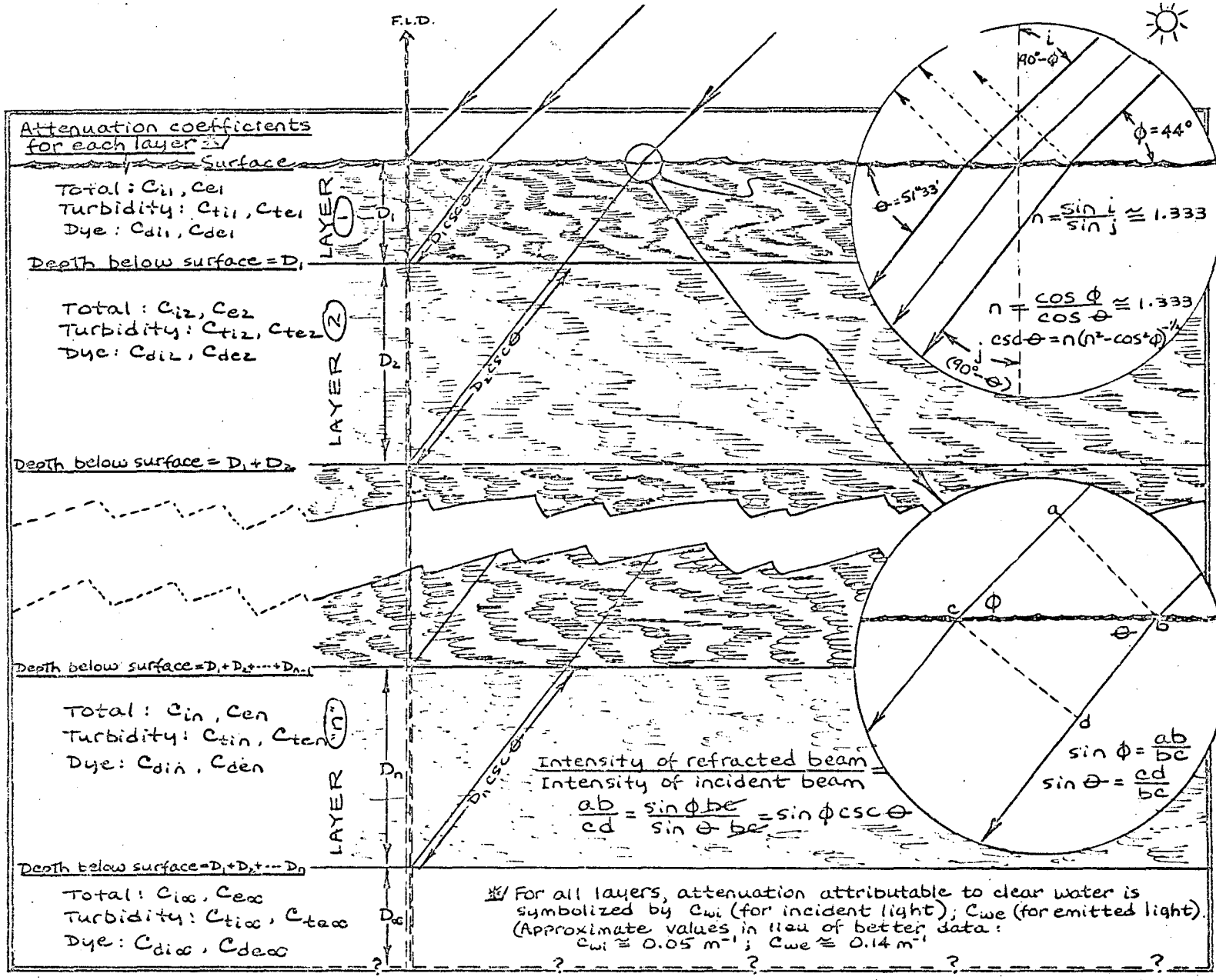


Fig. 2. Geometry applicable to sensing of solar-stimulated luminescence in marine environment by the F.L.D.

A suitable value for index of refraction is given by (Jerlov, N. G., 1968):

$$n \cong \frac{4}{3} \cong 1.333 \qquad (2)$$

The above value is used in succeeding calculations, although the value for blue-green light in sea water is more likely 1.334, the index varying slightly with temperature, wavelength, salinity, and turbidity (Jerlov, 1968). In sea water of temperature 20°C and salinity 3.5% the index is reportedly 1.334. Values also increase slightly with decreasing wavelength, from 1.333 at 5890Å (D_2 sodium line) to 1.335 at about 5350Å.

The relative intensities of the refracted and incident beams, in planes normal to the beams, should be inversely proportional to the ratio of the two beam widths, as shown on the lower inset of Figure 2:

$$\frac{\overline{ab}}{\overline{cd}} = \frac{\sin\phi\ \overline{bc}}{\sin\theta\ \overline{bc}} = \sin\phi\csc\theta \qquad (3)$$

in which: $\overline{ab}$ = width of incident beam

$\overline{cd}$ = width of corresponding refracted beam

The factor ($\sin\phi\csc\theta$) is included in the formula to compensate for loss in intensity of incident light, upon entering the water, as a result of reflection and of broadening due to refraction. In relation to the FLD, the problem is compounded by the fact that the incident light is measured in a complex manner. However the installation of a globe over the diffuser plate is designed to collect light in a manner nearly independent of sun angle, hence some compensating factor is necessary.

In conclusion, the following approximations involved in the treatment of incident light at and above the air-water interface may require further consideration in quantitative interpretation of FLD records:

1) Design of light collector may result in measure of light intensity that is a function of sun angle. Globe attachment is intended to compensate largely for this, but other modifications may be needed to eliminate dependence on sun angle.

2) Intensity of incident light (parameter A) is measured at yellow wavelength of 5892Å, while intensity of blue-green light at about 5540Å would be of greater value in this part of the problem. A correction factor should be considered, but more information is needed first on spectral distribution of incident sunlight and skylight under various lighting conditions.

3) Use of a globe attachment on the light collector, while partially solving the problem of variable light intensity, may introduce a new problem by collecting reflected light from side of the helicopter, particularly since the yellow color corresponds to the yellow spectral region sensed by the FLD. A black shield may be needed under collector.

4) Assumption that incident light intensity at sensor is the same as at water surface is an approximation. Factors most likely to interfere are probably cloud shadows, particularly cirrus cloud shadows, on sensor or water, and thin mist or sea fog near the water surface at certain times. Errors will have to be avoided by observing these visually.

5) Light reflected from clouds and sky contributes to light intensity sensed by light collector but in formula all incident light is treated as though it came from one direction. More information is needed on spectral distribution and intensity of light from sky and clouds.

6) Compensation for loss of incident light due to reflection from water is an approximation. An additional factor relating reflectivity to sun angle may be needed, but only in conjunction with such factors as

surface roughness, efficiency and angular dependence of light collector, and scatter, some of which may involve compensating errors.

7) Surface roughness of the water has been neglected. Magnitude of the possible error will need to be evaluated.

Treatment of light beneath the water surface

For simplicity, and as an approximation, all light beneath the water surface is treated as though it followed parallel paths and was attenuated strictly in accord with Beer's Law (Polcyn and Rollin, 1969). Scattering and absorption are treated together in the form of attenuation coefficients or transmittances, expressed as rates of attenuation of light intensity per meter or alternatively as transmittance per meter. Multiple paths followed by scattered rays have been overlooked, in accord with the numerous other approximations involved, and the difficulty of even estimating attenuation coefficients or transmittances. The relation between transmittance and attenuation coefficient is (Jerlov, 1968):

$$T = e^{-cr} \quad \text{(or)} \quad \log_e T = -cr \qquad (4)$$

in which: T = Total transmittance: the ratio of the transmitted radiant flux to the incident radiant flux (also may be expressed as % per meter, or transmittance rate, calculated by letting r be 1 meter)

e = Napierian base (2.7183...)

c = Total attenuation coefficient: the internal attenuance of an infinitesimally thin layer of the medium normal to the beam, divided by the thickness of the layer; expressed as meter^{-1} (reciprocal length)

r = Path-length of the beam (meters); in the FLD formula, (r) is replaced by path-lengths expressed in terms of depth beneath water surface (x), in meters.

By definition it is evident that attenuation coefficients operable along a light path are additive and that transmittance rates are factorial. In relation to function of the FLD, attenuation coefficients and transmittance rates are needed for two wavelengths of light and it is convenient to use separate symbols for three components of the medium (symbols are fully defined below only for attenuation coefficients; symbols for transmittance rates per meter are comparable):

$$C_i = C_{wi} + C_{ti} + C_{di} \quad (5)$$
$$(\text{alternatively } T_i = T_{wi} T_{ti} T_{di})$$

$$C_e = C_{we} + C_{te} + C_{de} \quad (6)$$
$$(\text{alternatively } T_e = T_{we} T_{te} T_{de})$$

in which: C_i = Attenuation coefficient for blue-green incident sunlight in spectral range from about 5400Å to about 5800Å; includes combined effect of absorption and scattering (meters^{-1})

C_e = Attenuation coefficient for yellow luminescence emission in vicinity of 5890Å (meters^{-1})

C_{wi}, C_{we} = Attenuation coefficients, as above, for distilled water

C_{ti}, C_{te} = Attenuation coefficients, as above, attributable to suspended sediment, coloring matter, impurities, but excluding effect of fluorescent dye.

C_{di}, C_{de} = Attenuation coefficients, as above, attributable to fluorescent dye (e.g., rhodamine WT dye)

T_i, T_e, T_{wi}, T_{we} . . . . (etc). Transmittance rates per meter

Referring to Figure 2, most light sensed by the FLD will have followed a diagonal path downward through the water until reaching the column beneath the instrument, and then a vertical path upward, assuming that the angle of view is vertical. It is evident that the path-length (r) of each light ray will be:

$$r = x \csc\theta \text{ (for incident light)}; \quad r = x \text{ (for emitted light)} \quad (7)$$

in which: x = variable depth beneath the water surface (meters) and therefore also path-length of emitted light rays

$x \csc\theta$ = path-length of incident light rays

Total transmittance (T) of radiant flux at the end of each of these path-lengths, bearing in mind the basic rationale described previously, which permitted actual intensity of incident radiant flux to be ignored (or assumed equal to unity), and which permitted the actual luminescence process to be treated as a separate factor later, will be equivalent to the product of the transmittance rate per meter for each meter of the path:

$$T = T_i^{x \csc\theta} T_e^{x} \tag{8}$$

Similarly, the total attenuation coefficient (C) for each path-length will be equivalent to the sum of all attenuation coefficients operative along the path:

$$C = C_i + C_e \tag{9}$$

Substituting (7), (8), and (9) in (4):

$$T_i^{x \csc\theta} T_e^{x} = e^{-x C_i \csc\theta} e^{-x C_e} = e^{-x (C_i \csc\theta + C_e)} \tag{10}$$

In the above, the transmittance rates (T_i and T_e) and the attenuation coefficients (C_i and C_e) each represent the combined effect of three constituents of the medium.

Since the FLD views a single water column, all of the light rays from the surface to depth (x) are integrated into one beam as sensed by the instrument:

$$\int_x^0 T_i^{x \csc\theta} T_e^{x} = \int_x^0 e^{-x (C_i \csc\theta + C_e)} \tag{11}$$

The right side is readily integrated. To facilitate integration of the left side it is convenient to assume that when the incident flux reaches the column sensed by the FLD, having traversed a path-length ($x \csc\theta$) along which a transmittance rate (T_i) was operative, some additional

attenuation of the light is necessary to reduce its intensity to the final level (T). It can be assumed that if the transmittance rate (T_i) continued to operate along the upward path of the emitted light, instead of the new rate (T_e), then there must be some hypothetical added path-length required in order for the light to attain the required final intensity (T) sensed by the FLD:

$$T_i^{\,z} = T_e^{\,x} \tag{12}$$

in which: z = hypothetical added path-length required to balance the equation

taking logarithms:

$$z \log T_i = x \log T_e \tag{13}$$

$$z = \frac{x \log T_e}{\log T_i} = x \log T_e (\log T_i)^{-1} \tag{14}$$

substituting (14) in (12):

$$T_e^{\,x} = T_i^{\,x \log T_e (\log T_i)^{-1}} \tag{15}$$

substituting (15) in (11) results in a form readily integrated:

$$\int_x^0 T_i^{\,x \csc\theta + x \log T_e (\log T_i)^{-1}} = \int_x^0 e^{-x(c_i \csc\theta + c_e)} \tag{16}$$

$$\left[\frac{T_i^{\,x \csc\theta + x \log T_e (\log T_i)^{-1}}}{\log_e T_i \left[\csc\theta + \log T_e (\log T_i)^{-1}\right]}\right]_x^0 = \left[\frac{e^{-x(c_i \csc\theta + c_e)}}{-(c_i \csc\theta + c_e)}\right]_x^0 \tag{17}$$

It is emphasized that the above represents the summation of the potential transmittances for all depths, while the actual transmittances will be related to the luminescence process and to all other factors operating to reduce the light intensity beneath the water surface.

In addition it has been assumed that transmittance rates and attenuation coefficients are uniform throughout the water column being sensed. These variations with depth will be considered later.

Treatment of factors related to attitude of the sensor

These factors include altitude of the aircraft, field-of-view of the FLD, angle-of-view of the FLD with respect to the water surface, and angle-of-view with respect to the refracted angle of incident light. These factors are considered in relation to angles of the light rather than absorption or attenuation in the atmosphere. It has been presumed that the aircraft is low enough that the basic assumption of quantitative sensing by the line-depth method is valid:- that the light at the target is equal in intensity and spectral distribution to the light at the sensor.

As the altitude of the aircraft increases, the field-of-view at the target will increase, but if the foregoing assumption is valid this should not have any effect on the amount of luminescence reaching the FLD, providing that the entire field of view is filled by the target. This results from the fact that luminescence emission is not collimated, but emanates equally in every direction from practically an infinite number of points. The field of view of the FLD is designed to be approximately 1 degree of arc, covering approximately a 1-foot circle at a distance of 60 feet and a 10-foot circle at a distance of 600 feet.

The angle of view has been assumed normal with respect to the water surface. If the angle varied from this it should have effects comparable to those affecting incident light at the air-water interface, but since the angle would presumably

vary as the plane moved these effects would continually change, introducing an unmanageable complexity into the computations, even if the angles were accurately known. If the viewing angle were subject to appreciable change with movement of the plane it would be preferable to do one of the following: 1) ignore those parts of the record where the viewing angle exceeded a few degrees; or 2) mount the instrument in such a way that the view stayed nearly vertical in the plane of maximum tilt, if such periods occurred with a frequency of more than about 10 percent of the time. The principal factors that relate to viewing angle are refraction of luminescence at the water surface, reflection of luminescence downward from the water surface or the nearly equivalent decrease in beam intensity on being refracted, and increased path-length of luminescence emission, resulting in increased attenuation.

It might conceivably be necessary to apply a constant correction for viewing angle if it were found after a series of tests that the instrument had been mounted at an angle over a tank of dye or on the side of an aircraft, or it might be desired to deliberately mount it at an angle along certain flight paths in order to avoid reflection from the water at certain sun angles. If a correction were needed it would be convenient to use the viewing angle below water (β) measured downward from the water surface and the angle above water (α) measured upward from the water surface. The luminescence intensity detectable by the FLD should then be reduced by an approximate factor ($\sin\alpha \csc\beta$) in crossing the air-water interface, in accord with equation (3), and the increased attenuation of emitted light should be compensated for by multiplying all transmittance rates and attenuation coefficients for emitted light by a factor ($\csc\beta$).

An additional angle not yet discussed is the angle-of-view with respect to the refracted angle of incident light. This angle can be seen intuitively to have no relation to the intensity of luminescence emission at the site of excitation. Because the dye in solution is translucent, all portions will be equally illuminated, for practical purposes, and the intensity of luminescence will be related only to the intensity of incident light normal to the beam. Of course the depth of the dye column sensed will vary with viewing angle, but this is an unrelated problem. This principle could have a practical application. It can be seen that a container of fluorescent dye being viewed by an airborne FLD will have a practically constant luminescence intensity as long as it is entirely within the field of view and as long as the intensity of incident light (normal to the beam) is unchanged. This means that such a container should be a nearly ideal means for monitoring solar intensity from a moving platform (plane or ship), being practically independent of both sun angle and platform angle.

Effect of water temperature, luminescence efficiency and instrumental sensitivity

These factors are all a function of either the concentration or the identity of the luminescent substance in the water. Therefore they are included in the general formula as unevaluated coefficients. Tentative values will be discussed in a later section in relation to the particular luminescent substance, which has been Rhodamine WT dye in tests performed to date.

In laboratory fluorometers the above factors are simply accounted for by using standards having a known concentration of the fluorescent substance and testing or correcting to the same temperature as the unknown sample.

The correction factors are applied by a simple graphical solution without requiring formulation or any mathematical calculation. Use of the FLD should follow a similar practice as far as practicable, bearing in mind that it is designed to be an airborne fluorometer.

Basically, every time the FLD is used as a quantitative sensor there will be a need for a standard and for some type of ground truth data, both of which are discussed later. It will be assumed that the temperature of the water column sensed by the FLD will either be known or approximated to within a few degrees Centigrade. Then a temperature correction coefficient applicable to many fluorescent solutes can be expressed as:

$$t_c = \left| \pm (t - t_s) \right|^{\mp m} u^{\pm 1} \qquad (18)$$

in which: t_c = water temperature correction coefficient, to be measured directly in tank tests, measured remotely (by radiometer, thermometer, or other device) during airborne use, or approximated from seasonal trends and available information if no measurements are possible

t = measured temperature (°C.) at time of test; if possible, should be temperature at mean depth of detectable luminescence sensed by FLD

t_s = temperature of standard (°C.) at time of calibration of FLD, i.e., at time of determination of value of S_c (defined below)

m = constant to be based on temperature dependence of the luminescence of the target material (derived from published curves and quantified for rhodamine WT dye in later section)

u = constant, as above

Only the absolute value of the difference between the two temperatures $|t-t_s|$ is to be included, but when the difference is positive it is placed in the denominator, in accord with the negative value of the exponent (m), and when negative is placed in the numerator. The formula for (t_c) was derived by mathematical analysis of published curves for the temperature dependence of three fluorescent dyes (Wilson, J.F., Jr., written commun. 1967) which showed the curves to be exponential. It is a characteristic of fluorescence that it increases with decreasing temperature because at low temperatures the incident radiation can be less efficiently transformed into thermal-generating movements.

Correction factors for luminescence efficiency and instrumental sensitivity are best accounted for by a factor which will be termed sensitivity correction coefficient (S_c). This will be determined by a standard target consisting of a cylinder of acrylic resin (lucite) filled with a known concentration of the fluorescent substance in solution and periodically held beneath the FLD. The standard will be used in a manner similar to the standard used by a fluorometer, and if the temperature could be adjusted to that of the water target, as in a fluorometer, this would be convenient in removing the need for temperature correction. In fact, this can be accomplished in tank tests by simply keeping the standard immersed in the tank of dye between uses. Comparable practises would be feasible if the FLD were ever used as a shipboard fluorometer. Strictly speaking, the sensitivity coefficient (S_c) should be considered to be the increment in rho produced by the luminescence from an infinitely small quantity of a luminescent solute divided by that quantity. The purpose is to remove any effect of depth

or concentration from calculation of the factor, leaving only the effect of intrinsic luminescence of the substance, and instrumental performance. For practical purposes, however, it will be most useful to think of the coefficient as containing an error factor, this being the factor necessary to balance the equation of calculated vs. measured rho values after all known factors have been considered. Therefore the coefficient will hopefully have the form:

$$S_c = aR \tag{19}$$

in which: S_c = sensitivity correction factor for FLD function and intrinsic luminosity of substance

R = concentration of the fluorescent substance

a = calibration constant (or error factor)

The above assumes that a direct proportionality will exist between measured and calculated values of rho for all concentrations of the fluorescent substance, permitting a constant correction factor. If this were consistently found to be true the value of (a), and therefore (S_c) could be determined by one or two standards. The greater the departure from direct proportionality the more standards will be needed to define the calibration curve and the more frequently the calibration will probably be required. Initial tests of the FLD over tanks of dye showed the value of (a) to be fairly constant for Rhodamine WT dye concentrations up to 55 ppb during tests lasting up to 1 hour. However the value of several attenuation coefficients used in calculating rho, and therefore used in calculating (S_c) and (a), were estimated and could be in error. These calculations are discussed later.

In laboratory fluorometers the calibration curve is generally very nearly a straight line, but also very commonly departs from this. Among the principal causes for departures from strict proportionality are failure to warm-up the instrument adequately. This same problem will be a major one in calibrating the FLD (i.e., in calculating S_c) because installation in a helicopter requires use of a 115-volt generator that cannot be started until the helicopter blades are turning. If a laboratory fluorometer had to be used in a similar manner it would be difficult to obtain reproducible results.

Treatment of multiple layers and changes with depth

Incorporation of factors from (3), (17), (18), and (19) permits a general formula for rho (the right side of equation #17 is used for simplicity); this assumes a single uniform surficial layer of the medium:

$$\rho = S_c t_c \sin\phi \csc\theta \left[\frac{e^{-x(C_i \csc\theta + C_e)}}{-(C_i \csc\theta + C_e)}\right]_x^0 \qquad (20)$$

$$\rho = \frac{S_c t_c \sin\phi \csc\theta \left[e^{-x(C_i \csc\theta + C_e)} - 1\right]}{-(C_i \csc\theta + C_e)} \qquad (21)$$

in which: x = depth below surface (meters) of lower limit of sensing (henceforth the symbol D will be used for constant depths)

Suppose that the depth of sensing by the FLD is unknown, but the water depth is presumed deeper than the greatest depth from which detectable luminescence emanates, and suppose also that the conditions present in the surficial layer continued uniformly throughout the column sensed by the FLD. Then the limiting depth (x) is effectively infinite (∞) and the luminescence coefficient sensed by the FLD would be:

$$\rho = \frac{S_c t_c \sin\phi \csc\theta}{C_i \csc\theta + C_e} \qquad (22)$$

The assumed uniformity of conditions with depth will not always exist , and in practise it may be necessary to treat the water column as a series of layers having differing values of fluorescent dye concentration, turbidity, attenuation coefficients, and possibly temperature. This type of subsurface data would almost certainly have to be obtained by lowering either sensors, targets, or sample-bottles to several depths at two or more times during each operational airborne test with the FLD. To keep computations within manageable proportions it would be well to treat the subsurface variations as though they occurred in two or three discrete horizontal layers, and whenever practicable the available data for each parameter would best be averaged over the water column sensed by the FLD, permitting the use of equation (22). This equation is the only one that lends itself readily to calculation of dye concentration (R), as shown later.

Figure 2 shows the designation of subsurface layers, each of which might have been defined in thickness by the spacing of water sample bottles. With increasing depth the thicknesses of the layers are designated D_1, D_2, . . . D_n and D_∞, the latter being a layer of indeterminate or unlimited thickness. Corresponding subscripts identify attenuation coefficients of each layer. In subsequent formulas (D) will reprsent a known depth, while (x) will continue to represent a variable depth.

At least two approaches seem to be possible in deriving formulas for the transmission of light through multiple layers, as applied to sensing by the FLD. The integrated transmittance from the surface to a finite depth (D) can in some cases be most conveniently treated as the integrated transmittance from the surface to infinite depth minus the integrated transmittance from depth (D) to infinity.

For two layers, the lower of indeterminate depth:

$$\rho = S_c t_c \sin\phi \csc\theta (e)\exp(-D_1 C_{i1} \csc\theta - D_1 C_{e1} - D_1 C_{i2} \csc\theta - D_1 C_{e2})(C_{i2}\csc\theta + C_{e2})\exp(-1) \quad (23)$$

For two or more layers, a separate temperature correction coefficient can be used for each layer, if available, and if there are significant differences. In these equations it is assumed available data are averaged to obtain a single value.

The general formula for function of the FLD over water targets consisting of any number of layers, the lowest of which is either of finite or indeterminate depth, is (note that terms enclosed in parentheses following "exp" are exponents of the term enclosed in parentheses preceeding "exp"):

$$\begin{aligned}
\rho = S_c t_c \sin\phi \csc\theta \Bigg[& \int_{x=D_1}^{x=0} (e)\exp(-x C_{i1}\csc\theta - x C_{e1})\,dx + \\
& (e)\exp(-D_1 C_{i1}\csc\theta - D_1 C_{e1}) \int_{x=D_1+D_2}^{x=D_1} (e)\exp(-x C_{i2}\csc\theta - x C_{e2})\,dx \\
& + (e)\exp(-D_1 C_{i1}\csc\theta - D_1 C_{e1})(e)\exp(-D_2 C_{i2}\csc\theta - D_2 C_{e2}) \\
& \cdots (e)\exp(-D_{(n-1)} C_{i(n-1)}\csc\theta - D_{(n-1)} C_{e(n-1)}) \int_{x=(D_1+D_2+\cdots+D_n)}^{x=(D_1+D_2+\cdots+D_{n-1})} (e)\exp(-x C_{in}\csc\theta - x C_{en})\,dx \\
& + (e)\exp(-D_1 C_{i1}\csc\theta - D_1 C_{e1})(e)\exp(-D_2 C_{i2}\csc\theta - D_2 C_{e2}) \cdots \\
& (e)\exp(-D_n C_{in}\csc\theta - D_n C_{en}) \int_{x=\infty}^{x=(D_1+D_2+\cdots+D_n)} (e)\exp(-x C_{i\infty}\csc\theta - x C_{e\infty})\,dx. \Bigg]
\end{aligned} \quad (24)$$

APPLICATION OF THE FRAUNHOFER LINE DISCRIMINATOR TO SENSING RHODAMINE WT DYE

Introduction

It was concluded previously that both quantitative and qualitative sensing of luminescence is of value but that the present FLD is designed to be a quantitative sensor. Foreseeable use will continue to be in sensing Rhodamine WT dye content. This requires that symbols used in the theoretical formulas derived in the previous section be evaluated. Factors that are a function of concentration need to be specifically related to the concentration of Rhodamine WT dye.

Almost every phase of the problem is intimately related to wavelength, the pertinent wavelengths being that at which the luminescence is sensed (5890 - 5892Å) and that of the incident light stimulating the luminescence. Tentative values for several parameters have been determined during initial tests of the FLD over tanks of Rhodamine WT dye solution in conjuction with determinations on a laboratory fluorometer. Others have been found in the published literature or estimated from available data, but several of the values used are suspect. Even in operational use it seem inevitable that more than one value will contain a considerable error. The most serious problem in evaluating parameters relating to Rhodamine WT dye has been the fact that it is a relatively new dye, the manufacturer has not divulged the chemical formula, and there seems to be practically no published information on its basic properties.

Rhodamine WT is reputed to be a stable and only slightly adsorptive dye that is superior to rhodamine B, but we have had problems making reproducible standard solutions of the dye, which may indicate deterioration. These problems are being investigated further. An alternative dye,

pontacyl pink, has been removed from the market. In addition to the need for definitive testing of the optical and other properties of Rhodamine WT dye, there is a need for better experimental data to improve most of the coefficients evaluated below.

Regarding the need for quantitative data, the following statements by Wilson and Kilpatrick (written commun., 1968) are appropriate:

> "It has been assumed in this manual that more complete information on the behavior of contaminants dispersing in a stream would be available from dye tracer tests than just travel rates or times. Should the latter be the only concern, the preparation of dye standards, the calibration of fluorometers, and careful fluorometric procedures would not be necessary. In fact the approximate definition of the dye cloud using fluorometer dial readings would be sufficient. The presentation of data in this form though is to be discouraged."

It has also been pointed out that dye concentrations "are necessary to assure that concentration values are below the maximum allowable levels prescribed in current policy statements, and for reporting purposes." (Wilson, J.F., Jr., 1967, written commun.)

Attenuation of light by clear water

Values for light attenuation by clear (distilled) water are useful for interpretation of tank tests in which clear tap water is used, or for interpretation of some tests using distilled water. The following values are used:

$$C_{wi} \cong 0.05\,m^{-1}\ ;\quad C_{we} \cong 0.14\,m^{-1} \qquad (25)$$

in which: C_{wi} = attenuation coefficient for clear water for blue-green incident sunlight in spectral range from about 5400Å to about 5800Å

C_{we} = attenuation coefficient for clear water for yellow luminescence emission in vicinity of 5890Å

The value for C_{wi} has been weighted somewhat in favor of wavelengths in

the lower half of the range. The values are probably close to correct for distilled water but probably should be raised from 0.03 m^{-1} to 0.05 m^{-1} for most tap water.

Although termed attenuation coefficients, which include both absorption and scattering, the total attenuation for clear water for wavelengths between 5500Å and 6000Å is probably from 98.5% to 99.5% attributable to absorption, and only 0.5% to 1.5% attributable to scattering (Jerlov, 1968). Since the error in the values is undoubtedly greater than this, the values might as well be termed absorption coefficients.

Attenuation of light by turbidity

Turbidity, as used in this report, includes all natural impurities in the water, such as suspended sediment, coloring matter, and organic matter. For interpretation of FLD records the effect of these constituents is best expressed in terms of their attenuation of light. Fluorescent dye artificially added to the water is excluded, as is the effect of the water itself.

In addition to its effects on the transmission of light, turbidity may influence luminescence emission in at least two ways: 1) by physical adsorption of dye by suspended sediment, which quenches its luminescence irreversibly; and 2) by chemical reaction with the dye, which also has an irreversable quenching effect. Some additional temporary quenching of luminescence is possible due to substances dissolved in the water. Until methods are devised quantifying the effect of impurities on both luminescence emission and light transmission, the most practicable treatment of turbidity seems to be by an attenuation coef-

ficient. The following values are anticipated, excluding the attenuation attributable to the clear water itself (Polcyn and Rollin, 1969):

For average ocean water: $C_{ti} \cong 0.05$; $C_{te} \cong 0.07\ m^{-1}$

For "clear" coastal water: $C_{ti} \cong 0.17$; $C_{te} \cong 0.19\ m^{-1}$

For average coastal water: $C_{ti} \cong 0.22$; $C_{te} \cong 0.26\ m^{-1}$ (26)

For turbid coastal water: $C_{ti} \cong 0.28$; $C_{te} \cong 0.30\ m^{-1}$

For very turbid water: $C_{ti} \cong 0.35$; $C_{te} \cong 0.37\ m^{-1}$

in which: C_{ti} = attenuation coefficients attributable to suspended sediment, coloring matter (excluding fluorescent dye), and organic matter for blue-green incident sunlight in spectral range from about 5400Å to about 5800Å

C_{te} = Attenuation coefficients attributable to suspended sediment, coloring matter (except dye) and organic matter for yellow luminescence emission in vicinity of 5890Å

The values of C_{ti} are weighted slightly in favor of the wavelengths in the lower half of the range in accord with the absorption peak for Rhodamine WT dye, which is at approximately 5570Å (Figure 1). It should be noted that water in rivers and estuaries, and occassionally in coastal regions off their mouths, attain much higher values. For example turbid water having an attenuation coefficient of 2 m^{-1} has been measured as far as 1 mile off the coast of Oregon and Washington, at the mouth of the Columbia River (Polcyn and Rollin, 1969).

Turbidity obviously is a serious problem in use of the FLD for measurement of fluorescent dye concentration, because small differences in turbidity, when integrated over the entire column sensed by the FLD, will result in very large differences in luminescence emission from the water surface. This also suggests, however, that if a standard slightly-submerged luminescent target were viewed by the FLD in turbid water, small differences in turbidity could readily be determined by the FLD. Such a target might consist of a fluorescent disc similar to the secchi-disc used by oceanographers to measure water clarity. It would need to be

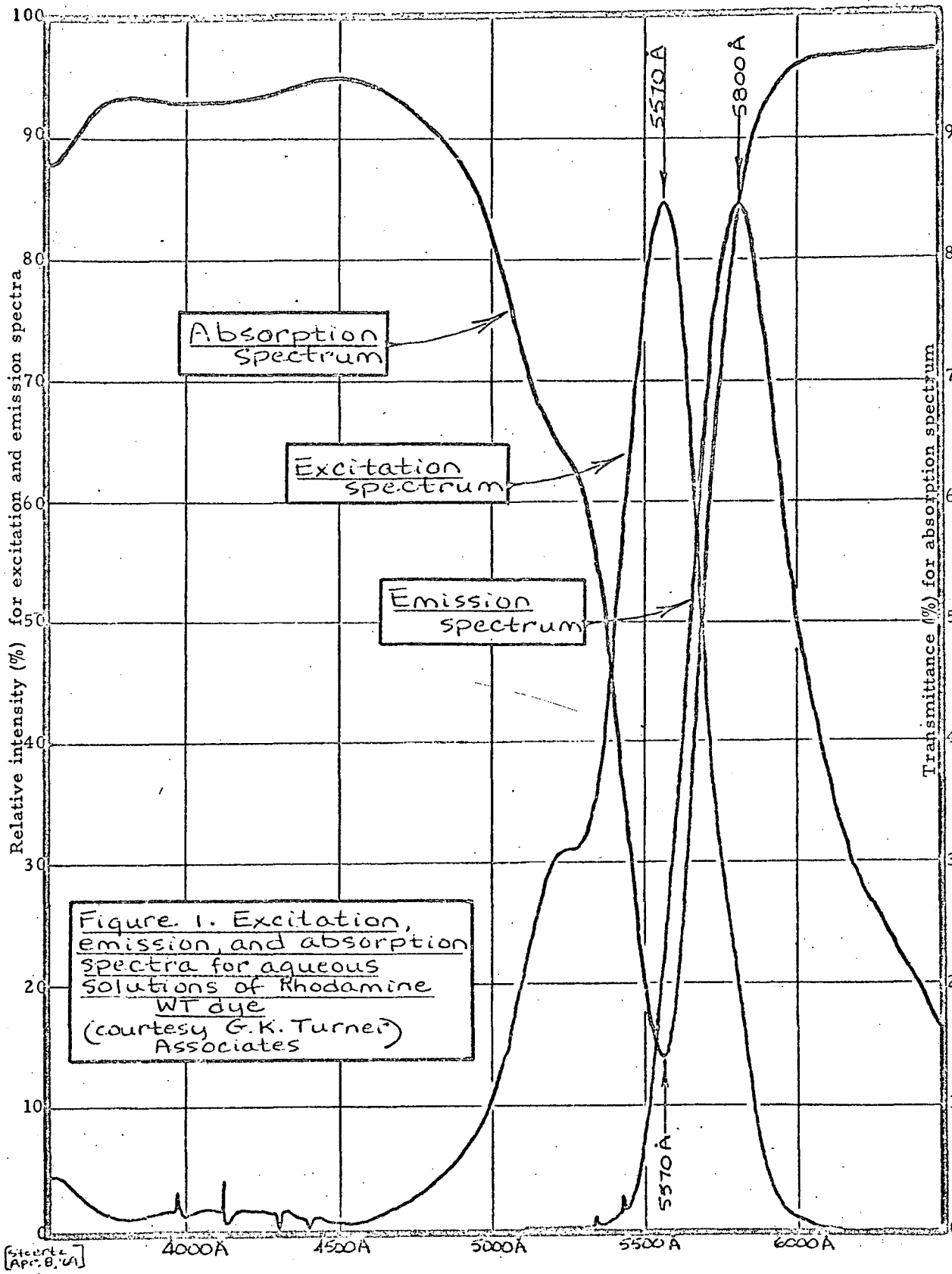


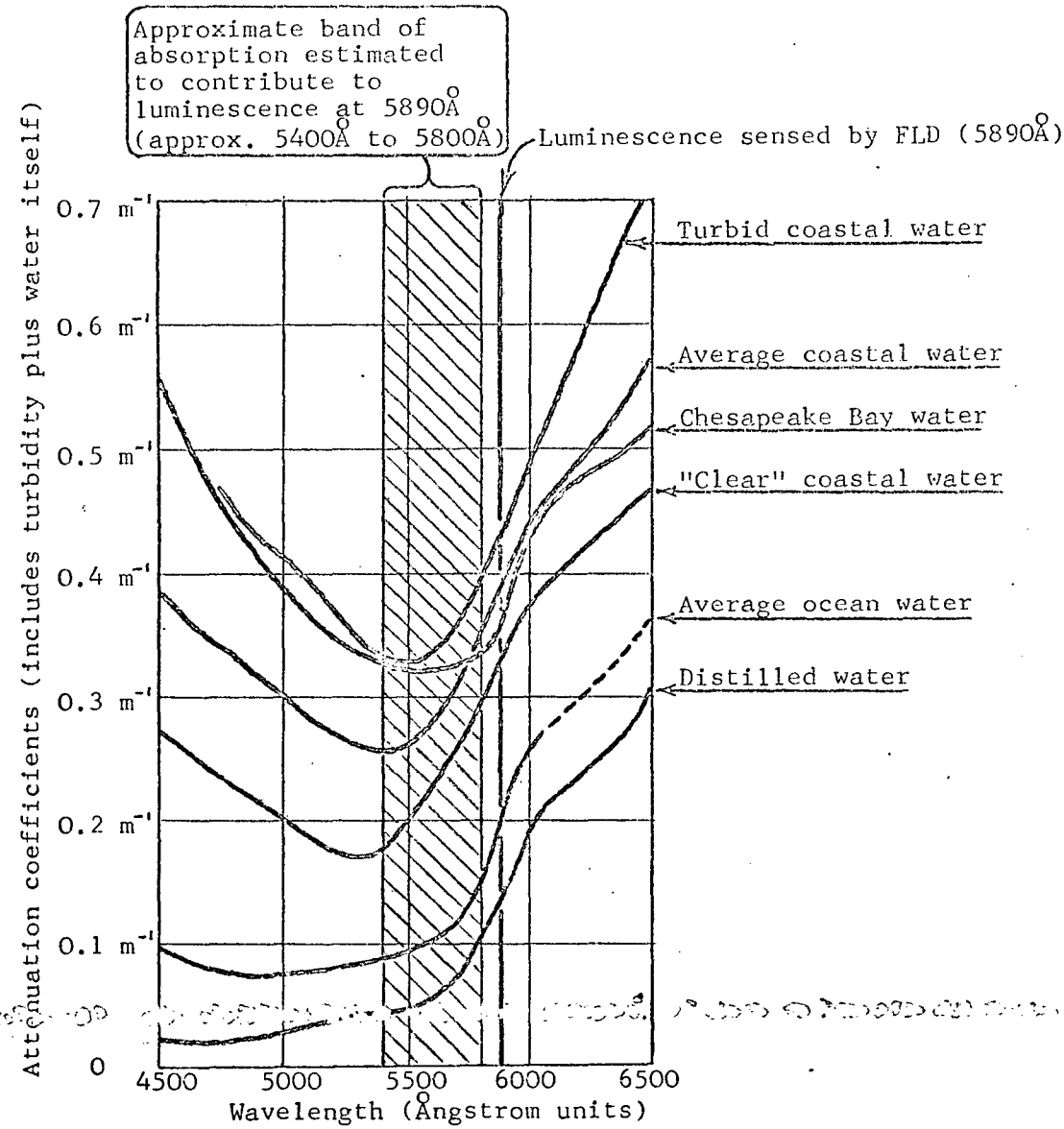
Figure 1. Excitation, emission, and absorption spectra for aqueous solutions of Rhodamine WT dye (courtesy G. K. Turner Associates

suspended at a fixed depth of perhaps 1 meter, be held down by a sinker and held up by a small float. It would need to be of known diameter (perhaps 2 feet), would need to be sensed when entirely within the field of view of the FLD, and when the FLD was at a known altitude above it. This would require the additional accesory of a sighting tube with cross-hairs, to determine the exact point at which the FLD is aimed and the approximate range.

By means of this or similar devices it is probable that the FLD will be able to obtain a rough measure of turbidity in the upper part of the water column, but all foreseeable methods will require some contact with the water surface, in effect, some ground-truth data.

It should be noted that the FLD, when used in conjunction with Rhodamine WT dye, is sensing in nearly the optimum part of the spectrum for penetration of turbid water, and the greater the turbidity the more nearly optimum this becomes. Maximum penetration (i.e., minimum attenuation) for the clearest water is in the blue part of the spectrum, as evidenced by the blue color of clear lakes (e.g., Lake Tahoe) and clear ocean water. As turbidity increases the maximum penetration shifts into the blue-green, the green, and the yellow-green, attaining even the yellow part of the spectrum in turbid flood-waters. The FLD used with Rhodamine WT dye would appear almost perfectly suited for achieving maximum penetration of typical Chesapeake Bay waters (Polcyn and Rollin, 1969) for example. These reportedly have minimum attenuation coefficients very close to the absorption peak of Rhodamine WT dye (5570Å), and the emission from the dye detectable by the FLD (at 5890Å) would also be in the lower part of the trough, as shown on Figure 3.

Figure 3. Wavelengths of light applicable to sensing of Rhodamine WT dye by the FLD, in relation to light penetration in turbid water (after Figure 7 in Polcyn and Rollin, 1969)



Attenuation of light by Rhodamine WT dye

Correct values for incident and emitted light attenuation by Rhodamine WT dye are critical, since they are a function of dye concentration, the parameter being measured by the FLD. There is a need for laboratory determination of certain optical properties of the dye which cannot be obtained from either the excitation, absorption, or emission spectra for the dye (Figure 1). To permit accurate use of the FLD there is a need for a very specific type of measurement that might actually be less difficult than measurement of complete spectra of the types mentioned. For known concentrations of Rhodamine WT dye in aqueous solution ranging from 0 to about 50 parts per billion, the intensity of luminescence emission at 5890Å to 5892Å should be measured while the excitation wavelength is varied over a spectral range from approximately 4500Å to 6000Å. This would produce an excitation spectrum relative to the specific wavelengths of 5890Å to 5892Å.

An additional type of measurement would also be extremely useful. This would be to obtain some measure of how the absorption or excitation wavelengths vary with depth in a solution. As the primary excitation band is depleted by absorption at overlying levels, do bordering bands, especially at shorter wavelengths, become increasingly effective, and to what degree ? The latter type of measurement would almost certainly require analysis in a spectrofluorometer that allowed variation of cell thicknesses from the 1 cm. standard generally used. For the time being it has been assumed that a broad band of wavelengths from approximately 5400Å to approximately 5800Å is actually effective in exciting luminescence emission of Rhodamine WT dye at 5890Å, but it seems most probable that the effective band-width varies at every depth in the solution and with every change in the intensity and spectral

distribution of the available light.

Tentative values to be used in interpretation of FLD records are listed below, and the basis for their estimation is explained more fully later, but they will need to be modified with better experimental data:

$$C_{di} \cong 0.0088\,R(m^{-1});\ C_{de} \cong 0.0006\,R(m^{-1}) \quad (27)$$

in which: C_{di} = attenuation coefficient attributable to Rhodamine WT dye in solution, for blue-green incident sunlight in spectral region from about 5400Å to about 5800Å

C_{de} = attenuation coefficient attributable to Rhodamine WT dye for yellow luminescence emission in vicinity of 5890Å

R = Rhodamine WT dye concentration (number of parts per billion, by weight)

The foregoing values are measured partly from curves (Figure 1) kindly run by G.K. Turner Associates on February 24, 1969, for Rhodamine WT dye in known concentrations, as follows (Phillips, R.E., written commun., Feb. 25, 1969):

1) Absorption spectrum: 3.5 ml. of 0.1% (by weight) of 20% solution per 100 ml. in water; concentration is:
$\frac{3.5}{100} \times 0.001 \times 0.2 = 7000$ ppb
2) Excitation and emission spectra: same, diluted 50-fold; concentration is:
$7000\ \text{ppb} / 50 = 140$ ppb

The absorption curve (Figure 1) represents values of absorptance (A): the ratio of the radiant flux lost from a beam by means of absorption, to the incident flux (Jerlov, N.G., 1968). The peak, at approximately 5570Å, represents an absorptance of roughly 0.85 within the standard cell thickness of 1 cm. In interpreting FLD records the parameter most applicable is attenuance, which includes both absorptance and scatterance (the ratio of the radiant flux scattered from a beam, to the incident flux). It is assumed that a negligible amount of scattering will be attributable to the Rhodamine

dye in solution, and that the absorptance of the dye is a fair measure of its attenuance.

It has also been assumed that, because of the great depths of solutions to be sensed, and the complete absorption of incident light that will occur within these depths, a broad band of incident light will be effective in stimulating luminescence at 5890Å, the band probably becoming broader as depth increases or as concentration increases. Therefore it was estimated that the effective average attenuation would be equivalent to a value of roughly 0.46 on the curve. Attenuance is the ratio of the radiant flux lost from a beam by means of absorption and scattering, to the incident flux, and therefore is given by (Jerlov, 1968):

$$1 - C = T; \quad T \cong 1 - 0.46 \cong 0.54 \tag{28}$$

applying equation (4):

$$\log_e T = -cr \tag{4}$$

$$\therefore c \cong \frac{0.616}{r} \cong \frac{0.616}{0.01\,m} \cong 61.6\,m^{-1} \tag{29}$$

The value equivalent to a concentration of 1 part per billion would therefore be:

$$\frac{61.6\,m^{-1}}{7000\,ppb} = 0.0088\,m^{-1}\,ppb^{-1}$$

If it is assumed that the absorption or attenuation is directly proportional to dye concentration (R) this can be expressed as:

$$c_{di} \cong 0.0088\,R\,(m^{-1}) \tag{27}$$

Until there is evidence to the contrary it will be assumed that there is a direct proportionality, otherwise the calculation of dye concentrations from rho measured by the FLD would involve three exponential functions of dye concentration, and the computation would be unmanageable. It has been concluded by many, if not most, workers that there is a direct proportionality between luminescence emission and dye concentration. A comparison of the curves on Figure 1 shows they are intimately related so that a departure from proportionality for emission would almost certainly imply a departure from proportionality for excitation and absorption. Available information on proportionality to dye concentration concerns chiefly emission, because of its importance in fluorescence assay. This problem may deserve further investigation since most published data seems to be based on short path-lengths of 1 cm. The phenomenon of "concentration quenching" is well known, consisting of a departure from direct proportionality for high concentrations. It may very well be found that the same phenomenon occurs in very deep solutions of low concentration, so that it might better be termed "absorption quenching", being more closely related to absorptance levels than to concentration levels. This is largely conjectural since previous work is not known to have been done on such deep solutions.

As early as 1904, Nichols and Merritt (1904) concluded: "Fluorescent substances having absorption bands of shorter wave-length than that with which the fluorescence is associated are capable of excitation by the absorbed light in each band, whatever its wave-length." The smoothly sloping curves characteristic of absorption, excitation, and emission spectra at normal temperatures must be attributable to this same principle,

so that the elimination of a narrow band of absorbed wavelengths would probably produce only a slight flattening in the contour of the emission spectrum.

It has been shown that there is a concentration dependence to the absorption spectra of aqueous solutions of fluorescein, eosin, and rhodamine B. Förster and König (1957) have suggested that dimerization of the dyes occurs in concentrated solutions. The monomer absorption peaks, upon dimerization, split into two peaks, one at slightly longer, the other at appreciably shorter wavelengths. In rhodamine B the phenomenon was found to occur at concentrations between 10^{-5} and 10^{-2} Mol/l, or roughly at concentrations above 10,000 parts per billion. With increasing concentrations in this range the prominent blue-green absorption peak shifts gradually from 5540Å to 5570Å or 5580Å (identical to the peak for Rhodamine WT), while decreasing from a relative intensity of absorptance of 0.96 to about 0.39, as shown on Figure 4. It is apparent that the absorption of Rhodamine WT dye should be investigated for comparable phenomena.

Temperature correction for Rhodamine WT dye emission

Values for constants to calculate temperature correction factor (t_c) for Rhodamine WT dye are:

$$m \cong 0.276 \; ; \qquad u \cong 1.38 \tag{30}$$

Substituting in equation (18), for Rhodamine WT:

$$t_c = \left| \pm (t - t_s) \right|^{\mp 0.276}{}_{1.38}{}^{\pm 1} \tag{31}$$

The formula would be useful for calculation of dye concentration on a computer, but for computation by hand a graphical correction may be preferable (Wilson, J.F., Jr., 1967, written communication), as on Figure 5.

Figure 4. Concentration dependence of absorption spectra of concentrated rhodamine B dye solutions

(from: Förster and König, 1957)

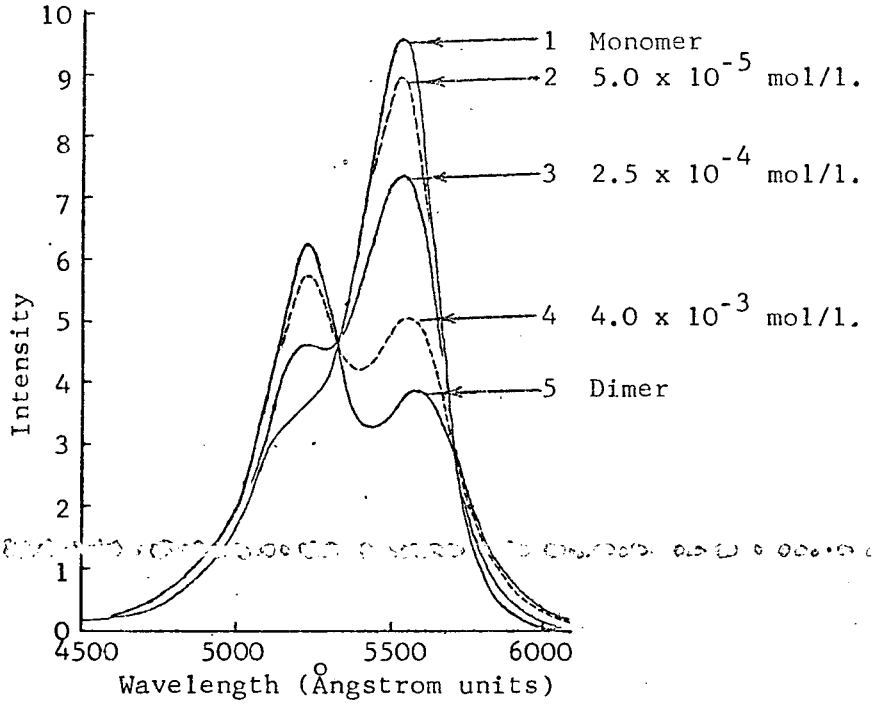


Figure 5. Graph for determining temperature correction coefficient (t_c) for sensing of Rhodamine WT dye by FLD

(from Wilson, J.F., Jr., 1967, written communication, Figure 13)

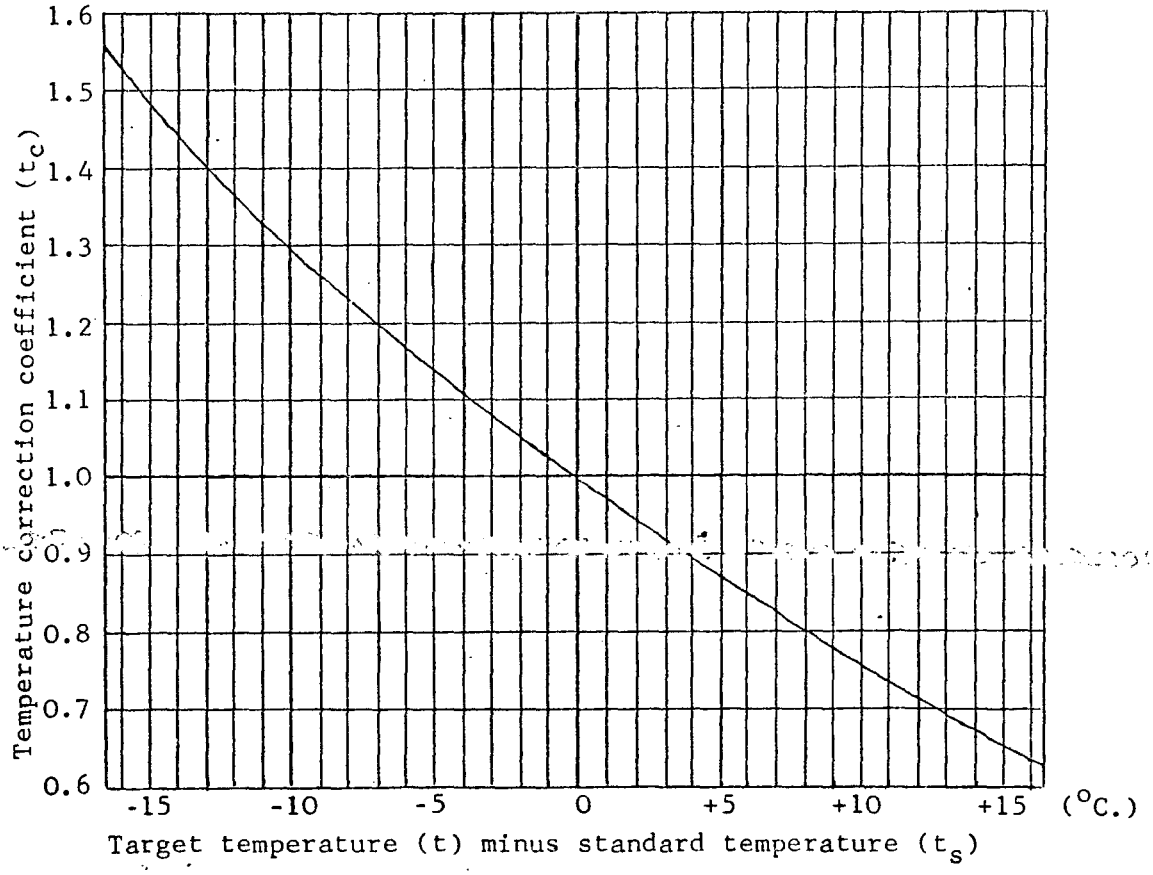
Procedure: 1. Measure temperature of standard used to calibrate FLD (t_s, °C.)

2. Determine or estimate target temperature (t, °C.)

3. Find ($t-t_s$) on graph

4. Find corresponding value of temperature correction coefficient on graph; if target temperature is higher, the value of t_c will be less than 1.0

5. Multiply t_c by computed value of rho



Equivalent formula: $t_c = \left|\pm(t-t_s)\right|^{\mp 0.276}_{1.38}{}^{\pm 1}$

Sensitivity correction for Rhodamine WT dye sensing

This will be determined every time the FLD is used, by calibrating with a standard. A convenient standard will be one for which all computations have been done in advance, requiring only temperature, sun angle, and rho value to be determined at time of calibration. However nearly any container of Rhodamine WT dye of known dilute concentration will be suitable. Calibration will then consist of computing rho by theoretical formula, comparing this value with the recorded value of rho, and finding the sensitivity correction coefficient (S_c) necessary to balance the equation.

An example of a procedure suitable for determination of (S_c) is shown on Table 1, but the values were applicable only on the day of the test (October 29). In this case a tank of liquid ½-meter deep was used, and the concentration of Rhodamine WT dye was varied from 0 to 55 parts per billion. It would be more convenient to use small standard containers filled with known dye concentrations.

The values of the correction coefficient (S_c) shown in column #20 vary with dye concentration. In a fluorometer calibration comparable values would be graphed against concentration to produce a calibration curve, from which unknown concentrations would be determined. This procedure depends on the fact that illumination angle, path-length of light (i.e., cell thickness), and temperature of sample are controlled and kept constant. In the use of the FLD these may vary, hence the more useful form of the calibration will be obtained by dividing (S_c) by dye concentration (R) to obtain a constant (a) and expressing (S_c) as a function of (R):

$$S_c = aR \; ; \qquad S_c \cong 0.0746\,R \tag{32}$$

Table 1. Example showing calibration of F.L.D. by determining sensitivity correction coefficient (S_c)

(determination based on values recorded October 29)

formula: $\rho = \dfrac{S_c t_c \sin\phi \csc\theta [e^{-x(c_i \csc\theta + c_e)} - 1]}{-(c_i \csc\theta + c_e)}$

#	Symbol or Operation	Notes: $t_c \cong 1.0$, therefore omitted from calculation; calculation used 4 signif. figures; nos. shown are rounded					
(1)	C_{di} (m^{-1})	0.044	0.13	0.22	0.31	0.40	0.48
(2)	C_{de} (m^{-1})	0.003	0.009	0.015	0.021	0.027	0.033
(3)	C_{wi} (m^{-1})	0.05	0.05	0.05	0.05	0.05	0.05
(4)	C_{we} (m^{-1})	0.14	0.14	0.14	0.14	0.14	0.14
(5)	$C_i = (1)+(3)$	0.09	0.18	0.27	0.36	0.45	0.53
(6)	$C_e = (2)+(4)$	0.143	0.149	0.155	0.161	0.167	0.173
(7)	$\csc\theta$	1.196	1.194	1.192	1.190	1.189	1.187
(8)	$C_i \csc\theta = (7)\cdot(5)$	0.112	0.217	0.322	0.426	0.535	0.634
(9)	$(8)+(6)$	0.255	0.366	0.477	0.587	0.702	0.807
(10)	$x\cdot(9) = 0.5\cdot(9)$	0.128	0.183	0.238	0.294	0.351	0.404
(11)	$\log_{10} e \cdot [-(10)]^*$	9.945	9.920	9.897	9.873	9.848	9.825
(12)	Antilog (11)	0.880	0.833	0.788	0.746	0.704	0.668
(13)	$-(9)$	-0.255	-0.366	-0.477	-0.587	-0.702	-0.807
(14)	$(12) - 1$	-0.120	-0.168	-0.212	-0.254	-0.296	-0.332
(15)	$(14)/(13)$	0.470	0.457	0.445	0.433	0.422	0.411
(16)	$\sin\phi \csc\theta$	0.816	0.818	0.821	0.823	0.825	0.826
(17)	$(16)\cdot(15)$	0.383	0.374	0.365	0.357	0.348	0.340
(18)	ρ (measured by FLD)	0.14	0.42	0.68	0.93	1.18	1.39
(19)	R (ppb)**	5	15	25	35	45	55
(20)	$(18)/(17) = S_c$	0.368	1.13	1.86	2.60	3.38	4.10
(21)	$S_c/R = (20)/(19)$	0.074	0.075	0.074	0.074	0.075	0.075

* (-10) omitted from logs. Average value: $S_c \cong 0.0746\ R$

** Concentration (R) plotted graphically from graph of measured rho values vs. concentration.

Suppose that the values of (S_c/R) as shown in Table 1 were not sufficiently close to express sensitivity coefficient (S_c) as a simple straight-line function of dye concentration (R). The most probable form of such a deviation would be such that the function was exponential:

$$S_c = aR^b \tag{33}$$

Because of the large number of factors on which the sensitivity depends, it is almost inevitable that an exponential function will occur on practically every day of use. It is also likely that the relation will be erratic and not subject to simple formulation. In these cases there are two alternatives to permit continued interpretation of the records in terms of dye concentration:

1) The curve of sensitivity correction (S_c) vs. dye concentration (R) of the standards can be plotted on a graph. An approximate formula can be written for portions of the curve having smooth uniform slopes in one direction. Emphasis should be on matching the portions of the curve in which testing is anticipated and the portions in which greatest accuracy is desired. In operational dye tests these will generally be the lowest concentrations detectable by the FLD, generally in the range from 0 to 10 parts per billion. However, if the formula is exponential it will make calculation of dye concentration nearly unmanageable. Therefore it would be preferable to match the lower portions of the curve (0 to 10 ppb) with the best-fitting straight-line function, and ignore the remainder of the curve, since the higher concentrations are generally of little importance in any case.

2) The second alternative would be to use the relations between sensitivity coefficient (S_c), dye concentration (R), and all other variables only as long as conditions remained unchanged, or as long as no new data were available from sampling or other ground-truth data. The relation of (S_c) to (R) (similar to equation #32) would then be incorporated into an empirical formula for dye concentration of the type to be derived below. One or more standards would then be used to re-define sensitivity (S_c) every time the conditions changed appreciably.

Calculation of Rhodamine WT dye concentration

In the case of sensing over deep water having sufficiently uniform conditions with depth that it can be considered a single layer of indeterminate or unlimited depth, and in turbid water where water depth exceeds the depth of sensing:

$$\rho = \frac{S_c t_e \sin\phi \csc\theta}{C_i \csc\theta + C_e} \tag{22}$$

Three parameters are a function of dye concentration (R), and assuming that these are straight-line functions:

$$S_c = aR \tag{32}$$

$$C_i = C_{wi} + C_{ti} + C_{di} = C_{wi} + C_{ti} + fR \tag{34}$$

$$C_e = C_{we} + C_{te} + C_{de} = C_{we} + C_{te} + hR \tag{35}$$

Substituting (32), (34), and (35) in (22):

$$\rho = \frac{Ra\,t_e \sin\phi \csc\theta}{Rf \csc\theta + Rh + C_{wi}\csc\theta + C_{ti}\csc\theta + C_{we} + C_{te}} \tag{36}$$

Solving for dye concentration (R):

$$R = \frac{\rho\left(C_{wi}\csc\theta + C_{ti}\csc\theta + C_{we} + C_{te}\right)}{a t_c \sin\phi \csc\theta - f\rho\csc\theta - h\rho} \quad (37)$$

Substituting tentative empirical values for the constants, that appeared valid in the test of October 29 (from Table 1):

$$R = \frac{\rho\left(0.05\csc\theta + C_{ti}\csc\theta + 0.14 + C_{te}\right)}{0.0746\, t_c \sin\phi\csc\theta - 0.0088\rho\csc\theta - 0.0006\rho} \quad (38)$$

Suppose that conditions allowed use of the above equation, and that sampling provided values for turbidity attenuation coefficients (C_{ti}, C_{te}) and temperature coefficient (t_c). Then dye concentration would relate only to luminescence coefficient (ρ) as long as sun angle (ϕ and θ) remained reasonably constant and as long as sensitivity coefficient (represented by 0.0746 R) remained constant. These conditions would probably be satisfied reasonably well for periods of 20 to 30 minutes, by using the sun angle at the mid-point. By graphing dye concentration vs. luminescence coefficient (ρ) for these conditions the dye concentrations could then be read directly from rho values. The alternative, if digital output of rho were available, would be to compute the values of dye concentration on an external computer at a later time, provided that levels of rho were also identifiable in real time to assist in determining course of the survey.

CONCLUSIONS

1) Initial tests of the FLD were made over aqueous solutions of fluorescent dye. Efforts to interpret these in terms of luminescence intensities or dye concentration made it evident that theoretical formulas for function of the FLD over water were necessary.

2) Recorded values of luminescence coefficient are approximately equivalent to the intensity of luminescence emission reaching the water surface, expressed in relation to the intensity of sunlight incident on the water surface.

3) A more meaningful definition of luminescence coefficient (rho) considers the entire water column sensed by the FLD: Rho is the relative intensity of upward-trending luminescence emission reaching the water surface from the column sensed by the FLD, after being attenuated by absorption and scattering by all constituents of the column (suspended sediment, the water itself, the dye itself, and other coloring matter).

4) The intensity of incident light sensed by the FLD and used in computation of rho is not the same as that stimulating the luminescence of the column sensed by the FLD. It is first depleted by refraction and reflection at the water surface and then attenuated by absorption and scattering.

5) Consequently rho is not equivalent to, nor even directly proportional to, intrinsic luminosity, but is dependent on a number of environmental factors unrelated to intrinsic luminosity. It had been concluded previously that rho is also dependent on instrumental factors, and is analogous to the dial reading of a fluorometer; rho might better be termed FLD reading.

6) Theoretical formulas have been derived relating these factors to rho, and several pertinent constants have been tentatively evaluated.

7) It would be particularly erroneous to interpret uncorrected rho values as a measure of relative levels of fluorescent dye concentration because a solution of 10 parts per billion (1 meter deep) might give the same rho value as 1 part per billion (10 meters deep).

8) Rho theoretically depends in part on several inderterminate factors that cannot be separately evaluated. It is convenient to combine these into a sensitivity coefficient (S_c) that can be evaluated periodically by means of standards, to relate instrumental sensitivity to increments of the fluorescent substance. It is almost inevitable that sensitivity coefficient will be related to dye concentration by an exponential function rather than a direct proportion.

9) The theory for computation of rho assumes that neither the instrument nor the water are partially or wholly in shadow, that the FLD is at a low altitude, and that the intervening atmosphere is reasonably free of absorptive or luminescent substances such as haze, fog, aerosols, or dust.

10) The foregoing conditions should be fulfilled on a normal clear sunny day with the FLD mounted in a helicopter, but the altitude limit remains to be determined. Errors will have to be avoided by visually observing such phenomena as cloud shadows, particularly cirrus cloud shadows, and thin mist or sea fog near the water surface, all of these imposing limitations on accuracy of the FLD.

11) To obtain meaningful data and to justify the specialized design

effort, it is essential to use the FLD as the quantitative sensor it was designed to be; a radically different design appears more appropriate for qualitative sensing. These are two alternative approaches to sensing and are fundamentally different, having different purposes, different applications, and different instrumentation.

12) The requirement for use of standards imposes the limitation that it must be known in advance what substance is the source of the luminescence emission. However detection of luminescence would not have that limitation.

13) A minor discrepancy in the theory of the FLD is that the measured sunlight intensity is in a different spectral region than the light stimulating the luminescence. This discrepancy cannot be readily compensated because it will vary with time of day, angle of sunlight, and amount of light reflected from sky and clouds. This is not likely to be a significant limitation, however.

14) An advantage of the FLD, when used in conjunction with Rhodamine WT dye, is that it is sensing in nearly the optimum part of the spectrum for penetration of turbid water, and the greater the turbidity the more nearly optimum this becomes (up to a level slightly more turbid than Chesapeake Bay).

15) A practical limitation in use of the FLD will probably be the need to re-define sensitivity (S_c) by viewing one or more standards every time conditions change appreciably. Basically, this coefficient

is the increment in rho produced by the luminescence from an infinitely small quantity of a luminescent solution divided by that quantity. The advantage will be that the coefficient also includes an error factor, to compensate for the cumulative error from several indeterminate sources.

16) There is a need for more information on the spectral distribution and intensity of incident sunlight and skylight under various conditions in order to correct for discrepancies in the theory.

17) Evaluation of the effect of surface roughness of the water is needed.

18) Further work is needed on testing the optical and other properties of Rhodamine WT dye in known concentrations, particularly any departures from direct proportionality to dye concentration.

19) It is recommended that efforts be made to explore methods of measuring approximate turbidity by means of the FLD, possibly by means of fluorescent discs similar to the secchi-discs used by oceanographers.

20) The possibility of computing dye concentration from rho values on an external computer should be explored, including conversion to digital output from the FLD.

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